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Growth and characterization of bismuth thiourea chloride (BTC)

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Abstract : Bismuth thiourea chloride (BTC) single crystals (red and yellow) were grown in sodium meta silicate gel at ambient temperature. The conditions for the growth of large size BTC single crystals were investigated. The crystal structure of red crystal was redetermined using single crystal X ray diffraction studies and found to be rhombohedral with space group $P\bar{3}$ and that of the yellow crystal to be triclinic with space group P1. Thermal analyses such as TGA and DSC indicate that the compound is thermally stable upto 140°C. The presence of sulphur-bismuth bonds in the complex has been revealed by Fourier transform infrared analysis. The hardness test was carried out using vicker's microhardness tester.

Keywords . Bismuth thiourea chloride (BTC), Gel growth; Morphology

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1. Introduction

Bismuth trichloride forms three kinds of adducts with thiourea [1-4] corresponding to the molar ratios 2:1 and 3:1. The second adduct occurs in two modifications as yellow [$3BiCl_3.7SC(NH_2)_2$] and red [$BiCl_3.3CS(NH_2)_2$]. The yellow crystal structure [5] shows the presence of two chemically nonequivalent bismuth atoms belonging to $[BiCl_5tu]^{2-}$ anions and binuclear $[Bi_2Cl_4tu_6]^{2+}$ cations. Coordination around metal is octahedral in all these ions and in the cations around metal is octahedral in all these ions and in the cations two octahedra share an edge as two chlorine ions are acting as bridges. The anionic parts of the red and yellow compounds have been compared based on the nearly regular octahedral environment of the metal atom. The comparison of bismuth coordination polyhedra for yellow and red crystals show that in both the lone pair exerts no stereochemical influence which is not unusual. The crystals are centrosymmetric with third order nonlinear susceptibilities. Since there is no detailed growth studies on both the red and yellow crystals of BTC, the present investigation deals with the growth of red and yellow crystals and characterization studies of the gel grown crystals by single crystal X-ray analysis, thermal analysis, FTIR, optical absorption studies and hardness studies.

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2. Experiment

BTC crystals are grown from gel using single diffusion technique. Sodium meta silicate (SMS) of density 1.04 g/cc, acidified with acetic acid is mixed with a solution of analar grade thiourea (inner reactant). The time for gelation is varied from 12 to 24 hours. Bismuth trichloride (99.99%) dissolved in 7N HCl is added as the outer reactant, diffuse into the gel medium and the following reaction takes place according to the equation,

$$BiCl_3 + 3CS(NH_2)_2 \rightarrow Bi[CS(NH_2)_2]_3Cl_3 \qquad (1)$$

The crystals are grown by varying the gel density, concentration of the inner and outer reactants. The gel density is varied between 1.03 and 1.06 g/cc and the pH is maintained at 5.5 throughout the experiment. Single crystal X-ray analysis was carried out using KM4CCD diffractometer, with graphite monochromater and MoK_α (0.71703 A) radiation. Powder X-ray analysis is carried out using Rich-Seifert diffractometer. Wavelength Dispersive X-ray Analysis (WDX) is carried out to confirm the elements present in the crystal. Thermogravimetric analysis (TGA) and Differential scanning calorimetric (DSC) analysis are carried out to investigate the thermal stability of the crystals. FTIR spectrum is recorded in the range 400 – 4000 cm^{-1} using Perkin-Elmer FT-IR spectrometer by KBr pellet

technique. Optical absorption spectrum is recorded for the crystals. Microhardness studies are carried out using Leitz diamond pyramidal indenter for loads varying from 5-100 g.

3. Results and discussion

The various parameters like pH, gel density, concentration of the reactants *etc.* are varied and the optimised condition for the growth of large, good quality crystals are found to be : pH – 1.04 g/cc, inner concentration (thiourea) – 2M and outer concentration ($BiCl_3$ in 7N HCl) – 1M. The dimensions of the red crystal is found to be 18 mm × 12 mm × 8mm and that of yellow crystal is 10 mm × 4 mm × 3 mm. The red crystals exhibit different morphologies such as hexagonal, hollow, prismatic and dendrites, which are not reported earlier [6]. The morphology of red crystal is shown in Figure 1. Figure 2 shows the as grown

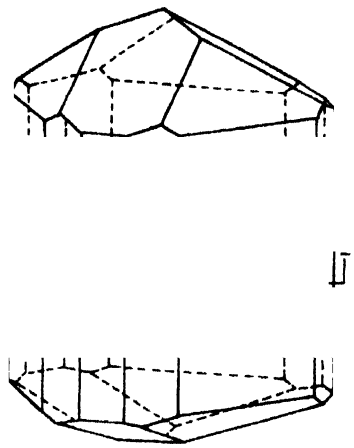

Figure 1. Morphology of BTC (red) crystal

Figure 2. As grown yellow crystal.

yellow crystal. Figure 3 shows the twinned crystal. Hollow crystals are found to grow at the interface. Figures 4 and 5 shows the hollow crystal with open lateral surface and hollow crystal with step-like structure. It is found that irrespective of the growth conditions, yellow crystals show prismatic morphology.

Single crystal X-ray investigation of red crystal showed the crystal structure to be rhombohedral with space group $P\bar{3}$ of unit cell parameters $a = b = 13.57(5)$ Å, $c = 7.13(9)$ Å; $V \doteq 1137.71$ Å^3; $\rho = 2.366$ g/cc [4]. The yellow crystal belongs to triclinic system with space group $P\bar{1}$ and the lattice parameters are found to be $a = 8.79(2)$ Å, $b = 16.17(2)$ Å, $c = 7.11(6)$ Å, $\alpha = 95.56(5)$, $\beta = 105.64(1)$ and $\gamma = 99.08(9)$ [5]. The single crystal data of the present investigation showed that the red BTC crystallizes with random disorder of thiourea molecules.

Figure 3. Twinned crystal

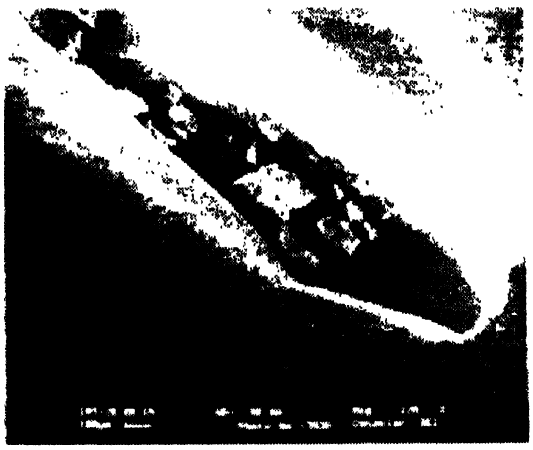

Figure 4. Open lateral surface of hollow crystal

Figure 5. Step-like layers inside the hollow crystal.

The thermogram of red (solid line) and yellow (dotted line) shown in Figure 6 illustrates the decomposition at three stages with maximum weight loss in the first stage starting at 218°C. The TGA curves of both red and yellow crystals show similar

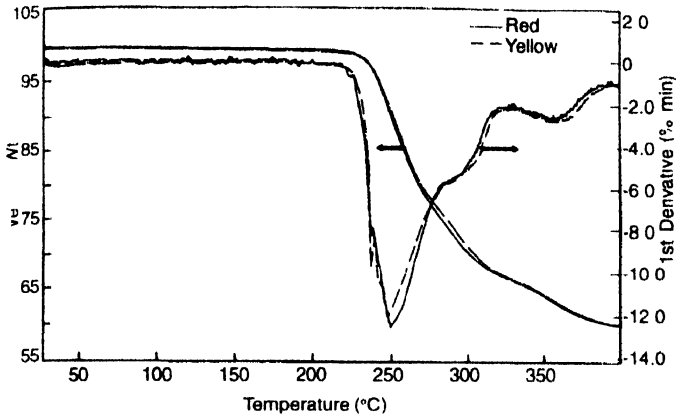

Figure 6. TGA curve of BTC

behaviour. There is no weight loss below 150°C indicating the absence of any entrapped moisture in the sample. The DSC trace is shown in Figure 7. Although the exothermic weight loss starting at 218°C coincides exactly with the weight loss observed in TGA, two endothermic peaks with maximum at 159.6°C and 193.3°C are observed. As the second peak is sharp, it is suspected to be melting. In order to confirm this, the sample has been separately tested for its melting point using Hot Stage Optical Microscope. The compound is observed to melt at 186°C supporting our presumption [4]. The higher melting point arises from a stronger bonding between the conjugation layers of thiourea molecules (which are planar) and the metal ion. This also influences the better mechanical properties and bulkier crystals with different growth habits. Hence, the first endotherm has been assigned to isomorphic transformation.

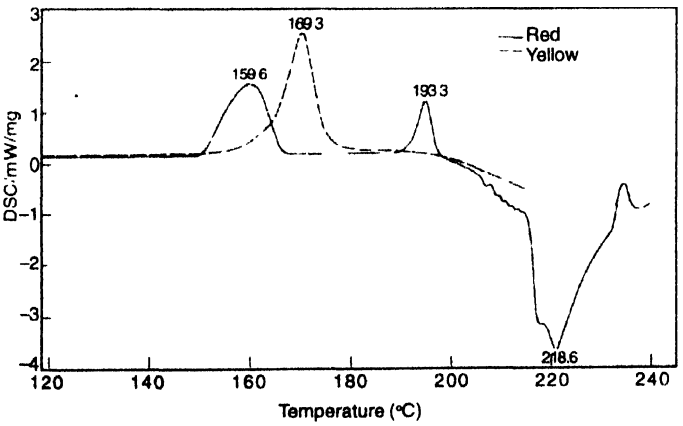

Figure 7. DSC curve of BTC

The elements present in the crystal are confirmed by Wavelength Dispersive X-ray analysis. The elements present in the crystal are found to be bismuth, sulphur and chlorine, which also confirm the absence of impurities such as Na, Si in the crystal.

Crystal structure investigation of thiourea has established the coplanarity structure of C, N and S atoms in the molecule [7-9]. The effect of metal coordination with thiourea complexes has not been studied extensively. The study of the spectra of thiourea [10] and BTC shows a shift in the frequency band in the low frequency range. Most of the metals form complexes with sulphur [11]. The structure of BTC reveals that Bi bonds with S. On complex formation with different types of ligands, the metal-sulphur peak is expected to lie in the lower wavelength region [12]. The absorption (Figure 8) at 464.8 cm^{-1} and 459

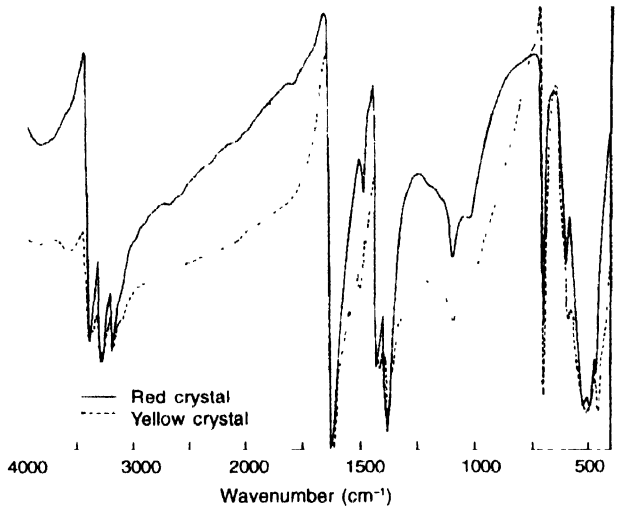

Figure 8. IR spectra of BTC

cm^{-1} for red and yellow crystals correspond to 469 cm^{-1} of thiourea which can be assigned to symmetric C = S stretching. The absorption at 491.8 cm^{-1} and 599.8 cm^{-1} for red BTC correspond to 480 cm^{-1} and 630 cm^{-1} of thiourea. This can be attributed to asymmetric N-C-N and N-C-S bending vibrations. The absorptions at 702 cm^{-1} and 700.1 cm^{-1} correspond to 720 cm^{-1} of thiourea. The lowering of frequency can be attributed to the reduced double bond character of C=S bond on coordination. The absorption at 1022.2 cm^{-1} and 1030.8 cm^{-1} correspond to 1010 cm^{-1} of thiourea which is due to NH_2 vibration. The absorption at 1097.4 cm^{-1}, 1377 cm^{-1} and 1093.6 cm^{-1}, 1375.2 cm^{-1} match with the 1090 cm^{-1} and 1390 cm^{-1} absorption of thiourea and can be assigned to symmetric CN stretching. The asymmetric C=S stretching results in absorption at 1431.1 cm^{-1} and 1413.7 cm^{-1} corresponding to 1420 cm^{-1} of thiourea. The absorption at 1627.8 cm^{-1} and 1612.4 cm^{-1} corresponding to 1625 cm^{-1} of thiourea can be assigned to NH_2 bending. The absorption at 3398.3 cm^{-1} and 3363.6 cm^{-1} match with 3295 cm^{-1} of thiourea which is due to asymmetric NH_2 stretching.

There is a strong interaction between bismuth and nitrogen in the case of red crystal due to less delocalisation of N_2 lone pair over C = S. Hence, C = S has more double bond character and has been shifted towards higher wave numbers compared to the yellow crystal. A comparison of vibrations of thiourea with those of red and yellow crystals is shown in Table 1.

Table 1. Assignment of FT-IR peaks.

Thiourea	BTC (R) cm^{-1}	BTC (Y) cm^{-1}	Assignment
469	464 8	459	δ_s (NCS)
480	491.8	-	δ_{as} (NCN)
630	599.8	-	δ_{as} (NCS)
720	702 0	700 1	γ_s (CS)
1010	1022.2	1030.8	τ (NH_2)
1090	1097 4	1093 6	γ_s (CN)
1390	1377 1	1375 2	γ (CN)
1420	1431 1	1413 7	γ_{as} (CS)
1625	1627 8	1612.4	δ (NH_2)
3295	3398 3	3363 6	γ_{as} (NH_2)

δ - bending vibration s - symmetric
τ non planar vibration as asymmetric
γ - stretching

The optical absorption spectrum of BTC single crystals is shown in Figure 9. The energy gap of the red crystal is calculated to be 2.25 eV and that of yellow crystal is calculated to be 2.38 eV which show that these crystals belong to wide bandgap semiconductors.

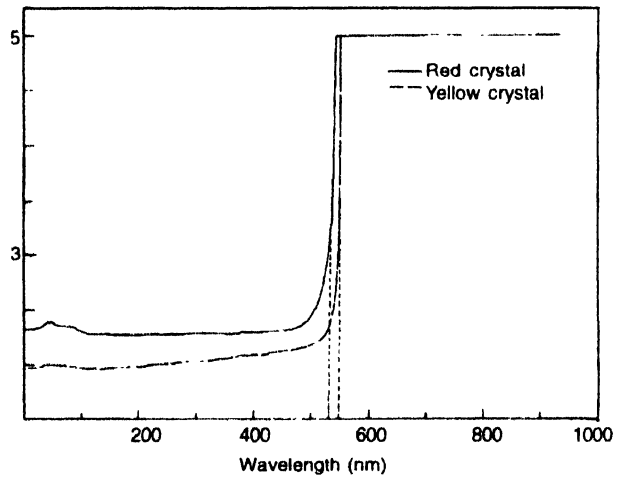

Figure 9. The optical absorption spectrum of BTC.

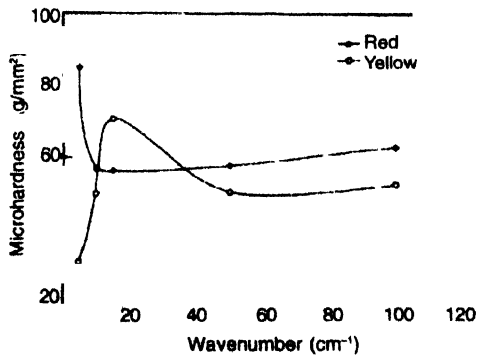

Figure 10. Variation of hardness with load.

The microhardness for the red crystal is found to be higher than the yellow crystals (Figure 10). The variation of hardness with load is also just opposite to each other showing the importance of bonding and difference in crystal structure.

4. Conclusions

BTC crystals were grown from gel. The conditions for the growth of large size single crystals were obtained. Single crystal X-ray analysis of the red crystal indicates it to be rhombohedral and the yellow crystal to be triclinic system. Thermal analyses of BTC showed that the compounds are stable in the solid-state but decompose on melting. IR studies showed that there is a shift in the frequency band in the low frequency region, which reveals that thiourea forms sulphur to bismuth bonds in the BTC crystal. Optical absorption studies showed that the compounds belong to wide band gap semiconductors. Hardness of red crystal is higher than the yellow crystal due to difference in crystal structure.

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